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Thermal expansion of some Cu-and Ag-base alloys at high temperatures.

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Using a 19cm Unicam high temperature camera and filtered CuK_α radiation from a stabilized Philips X-ray Generator photographs were taken of powders of Cu-Ni, Ag-Mn, Cu-Sn and Cu-In alloys in the solid solution range upto 500°C. In all these cases non-linear relationships were found between lattice parameter and temperatures. The linear thermal expansion coefficients were calculated from the lattice parameter-temperature curves and compared with the previously reported results. Attempts have also been made to explain the thermal expansion behaviours qualitatively.

Introduction

Recently, Rao *et al* (1964) have reported lattice expansion of some AgPd alloys using X-ray technique. They observed some sort of structural change in some alloy compositions which they explained to be due to temperature induced electronic structure change at higher temperatures. The present investigations deal with the X-ray method of thermal expansion measurements of some Cu- and Ag- base alloys with transitional and non-transitional solutes. Of all the substances studied, the most important is the Cu-Ni alloy system which like Ag-Pd alloys forms a continuous solid solution. From the investigations of different physical properties (Koster & Schule 1957 ; Ryan *et al* 1959 ; Schroder 1961 ; Rapp *et al* 1962) the presence of a miscibility gap (or clustering) has been suggested in this system. However, work on the enthalpies of formation of the electronically similar Ag-Pd alloys (Oriani & Murphy 1962) showed negative heats of formation suggesting the presence of a positive short-range order rather than a miscibility gap The similarity of the atomic scattering factors of the component metals Cu and Ni decreases considerably the sensitivity of both X-ray and neutron diffraction (Segre 1953) techniques to detect the presence of any such order. So it was hoped that at higher temperature the lattice parameter variation with temperature would indicate some sort of structural change present in different alloys of this system.

Besides Cu-Ni system, α- phase Ag-Mn alloys have also been investigated to study the effect of the transitional solute Mn on the thermal expansion of this system. For non-availability of any lattice parameter data at high temperatures it has also been considered desirable to extend

the work of thermal expasion to some other α-phase Cu- base alloys with non-transitional metal Sn and In as solutes.

Experimental Procedure

Cu-Ni alloys containing 26.54, 51.97 and 76.45 atomic percent of nickel were obtained from Messrs. Goldsmith Bros. (U.S.A.) as wires of 1.5mm. in diameter. Ag-Mn alloys with 5.54, 11.03 and 16.20 atomic percent of manganese, Cu-Sn alloys with 2.77, 5.11 and 7.98 atomic percent of tin and Cu-In alloys with 1.67, 5.16 and 6.19 atomic percent of indium were prepared from spectrographically standardized metals supplied by Messrs. Johnson, Matthey & Co., Ltd., London, following the same method as adopted previously (De 1967), the homogenization temperatures being 750-850°C. The annealing treatments were terminated by quenching in air. Weight changes during preparation being negligible no chemical analyses of the alloys were performed.

Preparations of the powder samples (about 4 mm in length and 0.5 mm in diameter) and mounting of the specimens on the specimen-holder were done in the usual way (De 1967) avoiding eccentricity. The standard 19 cm Unicam high temperature camera and filtered CuK_α radiation were used for taking the powder photographs at different temperatures lying between room temperature and 500°C. Any thermal gradient was minimised by taking very small specimens (as mentioned above) and by adjusting the controlling systems of the heating coils. Temperatures were measured within ± 1°C with the help of a pair of previously calibrated Pt-PtRh thermocouples. Room temperature photographs were taken at frequent intervals to check any effect of prolonged annealing and subsequent quenching on the specimens and also to detect any significant loss of the solutes by volatilization. No such effect was observed except with Cu-In alloys where volatilization of the solute was noticed at higher temperatures. To diminish the amount of volatilization, fresh samples were taken each time at higher temperatures but even this procedure failed for the Cu-6.19% In alloy above 350°C after which considerable decrease in the lattice parameter values was observed and this was mainly due to the loss of indium as verified by the subsequent room temperature photographs. Each photograph was followed by duplicate runs to show the reproduciblity of the data within the range of experimental error and the final value of the lattice parameter at any temperature given below is the mean of the results of two or more sets. The Cu-76.45% Ni alloy was studied in detail in the temperature range 70°—100°C giving temperature interval of 15°C. The lattice parameters were calculated from the line positions of the intense reflections (111), (200), (220), (311), (331)

α_1,α_2 and (420) α_1,α_2 and corrected by the standard extrapolation method of Taylor & Sinclair (1945).

Results

The lattice parameter values of the alloys at different temperatures are given in table 1 and are shown in figures 1 and 2 along with those for pure Cu (figure 2) from Mitra & Mitra (1963). By extrapolating the plots of the lattice parameter values against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$ to $\theta=90°$ (Nelson & Riley 1945) the accurate lattice parameter values at a particular temperature showed maximum deviations of $\pm$ 0.0003Å for Cu-Ni and Ag-Mn alloys and $\pm$ 0.0004Å for Cu-Sn and Cu-In alloys and these have been taken as the limits of accuracy. However, no correction due to refraction was applied since error due to refraction is much smaller than the experimental error.

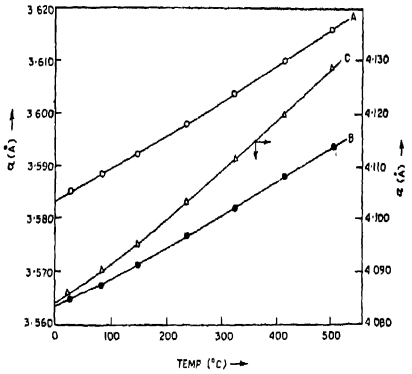

Figure 1a. Lattice parameter-temperature curves for Cu-Ni and Ag-Mn alloys. A : Cu-26.54% Ni , B : Cu-51.97% Ni ; C : Ag-5.54% Mn.

From figures 1 and 2 it is found that the lattice parameter values increase with the increase of solute concentration and the lattice parameter versus temperature plots show smooth non-linear curves concave upwards. The lattice parameter-temperature curve for the Cu-76.45%Ni alloy (figure 1b), however, shows a discontinuity at about 90°C and at higher temperatures this curve is more or less linear. Some of these curves can best be represented by the following types of equations :

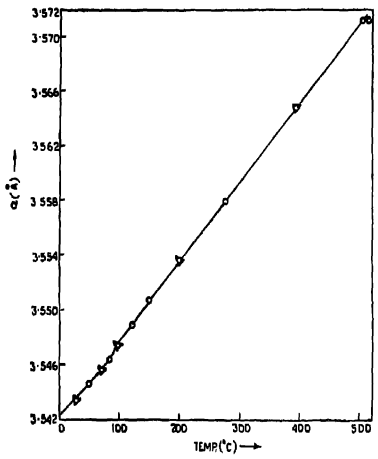

Figure 1b. Lattice parameter-temperature curve for Cu-76.45% Ni alloy.

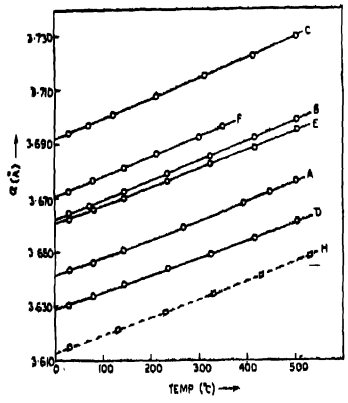

Figure 2 Lattice parameter-temperature curves for pure Cu, Cu-Sn and Cu-In alloys
A : Cu-2.77% Sn ; B : Cu-5.11% Sn ; C : Cu-7.98% Sn ;
D : Cu-1.67% In ; E : Cu-5.16% In ; F : Cu-6.19% In ;
H : Pure Cu.

(i) For Cu-5.11% Sn :

$$a_T = 3.66232 + 6.774 \times 10^{-5}T + 1.690 \times 10^{-8}T^2 - 1.624 \times 10^{-11}T^3$$

(ii) For Cu-7.98% Sn :

$$a_T = 3.69196 + 7.393 \times 10^{-5}T + 2.866 \times 10^{-10}T^2 + 4.828 \times 10^{-12}T^3$$

(iii) For Cu-1.67% In :

$$a_T = 3.62888 + 6.068 \times 10^{-5}T + 5.473 \times 10^{-11}T^2 + 1.485 \times 10^{-12}T^3$$

(iv) For Cu-5.16% In :

$$a_T = 3.66071 + 6.323 \times 10^{-5}T + 12.302 \times 10^{-9}T^2 - 4.219 \times 10^{-12}T^3$$

(v) For Ag-5.54% Mn :

$$a_T = 4.0842 + 6.948 \times 10^{-5}T + 4.425 \times 10^{-8}T^2 - 1.357 \times 10^{-11}T^3$$

where a_T =lattice parameter at T°C.

The room temerature lattice parameter values, measured frequently in course of the experiments, showed no changes greater than the experimental error. These values are also compared with those obtained by interpolation from the measurememts of (i) Coles (1956) for Cu-Ni alloys, (ii) Raub & Engel (1946) for Ag-Mn alloys, (iii) Owen & Iball (1935), Guljaev & Trusova (1950) for Cu-Sn alloys and (iv) Jones & Owen (1954) for Cu-In alloys. The mean and maximum differences were found to be 0.0005 and 0.001Å for Cu-Ni alloys, 0.0003 and 0.0006Å for Ag-Mn alloys 0.0004 and 0.001Å for Cu-Sn alloys and 0.0003 and 0.0008Å for Cu-In alloys. However, the purity of the substances is not of the same order in all the cases and a difference of nearly 10—12°C exists between these room temperatures. Also, difference in lattice defects, if any, due to differences in residuals trains may, to some extent, change the lattice parameter values.

TABLE 1. LATTICE PARAMETER-TEMPERATURE DATA FOR Cu-Ni, Ag-Mn, Cu-Sn AND Cu-In ALLOYS.

Cu-26.54% Ni Alloy		Cu-51.97% Ni Alloy		Cu-76.45% Ni Alloy	
Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)
29	3.5850	28	3.5650	27	3.5434
84	3.5885	84	3.5678	50	3.5446
148	3.5924	148	3.5714	71	3.5457
236	3.5980	236	3.5768	84	3.5464
324	3.6037	324	3.5822	97	3.5475
416	3.6098	416	3.5879	120	3.5489
505	3.6158	505	3.5935	148	3.5507
				200	3.5536
				275	3.5580
				393	3.5649
				505	3.5715

TABLE 1 *(Contd.)*

Ag-5.54% Mn Alloy		Ag-11.03% Mn Alloy		Ag-16.20% Mn Alloy	
Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)
24	4.0860	24	4 0858	24	4.0854
84	4.0904	84	4 0903	84	4.0900
148	4.0952	148	4.0960	148	4.0962
236	4.1032	236	4.1042	236	4.1040
324	4.1112	324	4.1120	324	4.1124
416	4.1195	416	4.1204	416	4.1204
505	4.1286	505	4.1284	505	4.1288
Cu-2.77% Sn Alloy		**Cu-5.11% Sn Alloy**		**Cu-7.98% Sn Alloy**	
Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)
31	3 6432	29	3.6644	30	3.6940
80	3.6463	72	3.6672	72	3.6972
144	3.6505	144	3.6724	122	3.7013
274	3.6592	236	3.6791	212	3.7082
393	3.6677	324	3.6856	312	3.7149
450	3.6718	416	3.6922	416	3.7227
505	3.6758	505	3 6986	505	3.7299
Cu-1.67% In Alloy		**Cu-5.16% In Alloy**		**Cu-6.19% In Alloy**	
Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)	Temp. (°C)	Lattice parameter (Å)
30	3.6306	30	3.6626	30	3.6727
80	3.6338	80	3.6658	80	3.6763
144	3.6378	144	3.6700	144	3.6809
236	3.6436	236	3.6762	212	3 6860
324	3.6492	324	3.6825	300	3.6924
416	3.6552	416	3.6888	350	3.6963
505	3.6611	505	3.6950		

From figures 1 and 2 the linear thermal expansion coefficients α were determined from the relation, $\alpha = 1/a \frac{da}{dT}$ taking different temperature intervals and are plotted in figures 3 and 4. The α values for pure Cu measured with a quartz dilatometer by Leksina & Novikova (1963) and those for Ni measured with an interferometric dilatometer by Nix & Macnair (1941) are also shown in figure 3 for comparison. In figure 4, the thermal expansion of pure Cu from Mitra & Mitra (1963) using X-ray tecnhique has also been indicated along with the dilatometric measurements of Leksina & Novikova (1963) and it seems that at higher temperatures X-ray

method gives higher values of α than those by dilatometric method. However, the present measurements with several alloys show the consistency in the α values increasing nonlinearly with temperature. For Cu-Ni alloys this non-linearity is greater for alloys with higher nickel concentration and for Cu-76.45% Ni alloy a break occurs in the α-T curve near 90°C (figure 3). The graphical method of determining the α values by taking equal temperature intervals for some alloy compositions introduces some uncertainties in the values of da/dT and hence in α. But the smooth curves drawn through the experimental points remove these uncertainties and represent the correct temperature variation of α. The maximum fluctuation of the experimental value of α at any particular temperature from its corresponding value obtained from the smooth curve was estimated to be within 3%.

Discussion

In case of alloys, Owen & Roberts (1939), Quader & Dey (1962) and Rao *et al* (1964) obtained these types of nonlinear curves from the lattice parameter-temperature plots of some other Cu-and Ag- base alloys. The interpretation for this nonlinearity, however, seems to be difficult with the present knowledge of lattice dynamics of alloys. Generally any change in the slope of the lattice parameter- temperature curves may be associated with changes in the magnetic states, short-range order and/or the electronic structure such as overlapping of Brillouin zones (Busk 1952). The vacancy concentration at higher temperatures may also cause some change in the slopes of the a-T curves. Any significant effect of the latter is, however, unlikely in these cases because the highest temperature studied is much below the melting points of the alloys. Since the room temperature lattice parameter values remained unchanged even after long annealing at higher temperatures and subsequent quenching in the camera, there is hardly any possibility of the presence of short-range order. As regards the influence of any change in the magnetic properties, all the alloy compositions, except the Cu-76. 45% Ni alloy, being paramagnetic in this temperature range, may have very feeble magnetic interaction so as to produce no significant effect on the a-T curves. However, the presence of any ferromagnetic clusters in the Ni rich alloys of the Cu-Ni system (Ryan *et al* 1959; Schroder 1961) may influence the a-T curves to some extent. The discontinuity near about 90°C in the a-T curve of the Cu-76.45% Ni alloy (figure 1b) is probably related to magnetic ordering since this alloy is ferromagnetic below this temperature. Cu-Ni and Ag-Mn alloys may also have some temperature induced electronic structure change due to low degeneracy temperature of the incomplete d-shell electrons and at higher temperatures increase of holes in the d-band may change the lattice structure so as to introduce some non-linearity in the a-T curves of these alloys. Similar

behaviours were also observed in some compositions of Ag-Pd alloys (Rao *et al* 1964). In the cases of Cu-Sn and Cu-In alloys such electronic structure change is, however, unlikely.

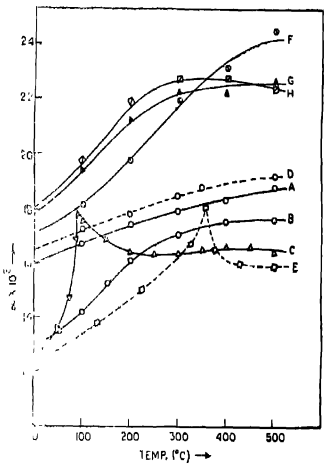

Figure 3. Linear thermal expansion coefficients α against temperature curves for Cu, Ni, Cu-Ni and Ag-Mn alloys.

A : Cu-26.54% Ni ; B : Cu-51.97% Ni ; C : Cu-76.45% Ni ;
D : Pure Cu ; E : Pure Ni ; F : Ag-5.54% Mn
G : Ag-11.03% Mn H : Ag-16.20% Mn.

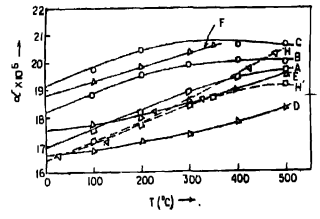

Figure 4. Linear thermal expansion coefficients α against temperature curves for Cu, Cu-Sn and Cu-In alloys

A : Cu-2.77% Sn ; B : Cu-5.11% Sn ; C : Cu-7.98% Sn ;
D : Cu-1.67% In ; E : Cu-5.16% In ; F : Cu-6.19% In ;
H ; Pure Cu (X-ray method) ; H' : Pure Cu (Dilatometric method)

From figures 3 and 4 it is found that in general, the expansion coefficients α increase with the increase of temperature and concentration of the solutes—the Cu-Ni alloy system being the only exception where the α values decrease with the increase of the solute concentration (figure 3). Figure 3 also shows that in the Cu-Ni system the α-T variation for the Cu-rich alloy is similar to that for pure Cu (Leksina & Novikova 1963) whereas, the Ni-rich alloy has this variation similar to that for pure Ni (Nix & Macnair 1941). The literature (Smithels 1962) reports the room temperature α value for Cu-45 wt.% Ni to be 14.9×10^{-6}/°C and from the present measurements this value is 14.3×10^{-6}/°C for Cu-50 wt. % Ni (i.e. Cu-51.97 atomic percent Ni) alloy. The striking feature of the Cu-Ni system is the increasing nonlinearity of the α-T curves with the increase of Ni concentration which is probably due to the increasing electronic and magnetic contribution to the thermal expansion. The increasing nonlinearity in the α-T curves of Ag-Mn alloys also supports higher electronic contribution to the thermal expansion with the increase of manganese concentration. The behaviour of the thermal coefficient of expansion in the Cu-76.45% Ni is obscured by the presence of a volume change accompanying the vanishing of ferromagnetism with the result of formation of a peak at about 90°C which is the Curie point of this composition. However, the presence of small amounts of impurities in ferromagnetic substances can play a dominating role in determining the total thermal expansion near Curie point (Williams 1934; White 1961).

From figure 4 it is found that in the cases of Cu-Sn and Cu-In alloys the expansion coefficients α increase slowly with temperature and concentration of the solutes. The room temperature α value for Cu-2.77% Sn alloy is of the order of 17.4×10^{-6}/°C. Hidnert (1943) reported a room temperature α value for Cu-1.3% Sn alloy to be 16.8×10^{-6}/°C.

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